

Determination of Th, U and K in ultrapure Li₂CO₃ by Inductively Coupled Plasma Mass Spectrometry for neutrino-less double beta decay experiment

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Abstract

Li₂CO₃, a raw material of Li₂MoO₄ crystal used for searching the neutrino-less double beta decay ($0\nu\beta\beta$), must be of high purity and low content of Th, U and K. In this study, quantitative methods were developed to determinate the content of Th, U and K in ultrapure Li₂CO₃ samples by inductively coupled plasma mass spectrometry (ICP-MS). The research showed the signals of Th, U and K were significantly inhibited with the increasing of lithium concentration. When the lithium concentration reached 8000 ug g⁻¹, the recovery of Th, U and K decreased to 10 ~ 30 %. For the determination of Th and U, both the recovery correction method and the TEVA - UTEVA combined resin method can eliminate the influence of the lithium matrix. The recovery correction method was simpler to operate, while the TEVA - UTEVA combined resin method was lower in detection limit. For measurement of K, the plasma gas (Ar) in the ICP - MS also induced significant interference. Compared with the standard measurement mode of ICP - MS, the cold flame mode with reduced radio frequency (RF) power can effectively reduce the interference from Ar, greatly

improving the detection sensitivity of K. Meanwhile, the detection limit of K in Li_2CO_3 samples can be as low as 7.53 ng g^{-1} , correcting the inhibitory effect of the lithium matrix by the recovery correction method. A neutron activation analysis (NAA) measurement was also performed for the comparison, yielding results consistent with ICP-MS.

Keywords

Th U and K, Li_2CO_3 , Li_2MoO_4 crystal detector, Quantitative method, Neutrino-less double beta decay

Introduction

Searching for the neutrino-less double beta decay ($0\nu\beta\beta$) is now regarded as the topmost promising routine to explore the mysterious nature of neutrinos after the discovery of neutrino masses in oscillation experiments. After several decades of development, the international large-scale $0\nu\beta\beta$ experiments can be divided into several technical routines, such as GERDA [1], MAJORANA [2], LEGEND [3] using high-purity germanium detectors, KamLAND-Zen [4] using liquid scintillator, EXO-200 [5], nEXO [6] using liquid xenon time projection chamber (TPC), NEXT [7], PandaX-III [8], NvDEx [9] using high-pressure gas TPC, and CUORE [10], CUPID [11] using Cryogenic crystal bolometer. CUORE (Cryogenic Underground Observatory for Rare Events) is a ton-scale cryogenic detector located at Laboratori Nazionali del Gran Sasso (LNGS) in Italy searching for $0\nu\beta\beta$ decay in ^{130}Te . At present, the CUORE experimental background level is $(1.38 \pm 0.07) \times 10^{-2}$ counts/(keV.kg.year) in the $0\nu\beta\beta$ decay region of interest [12]. CUPID, CUORE Upgrade with Particle Identification, will search for the $0\nu\beta\beta$ of ^{100}Mo and expect to reduce background noise of two orders of magnitude by optical and thermal dual channel readout [13,14]. Li_2MoO_4 crystal is considered to be a good candidate because it has a high Q value, a high concentration of molybdenum (55 wt%) and relatively easy to grow [15].

To avoid interference from natural cosmic rays, the detector must be placed deep underground [16]. In addition, all materials selected for the detector must be of high purity, especially with regard to the content of Th, U and K in the materials [17,18]. The decay of Th, U and their daughter products can generate gamma rays similar to those in the neutrino-less double decay, increasing the background of the detector [19-21]. As the main raw material for Li_2MoO_4 crystal preparation, the contents of Th, U and K in Li_2CO_3 should be also strictly controlled.

There are several quantitative analytical techniques for material purity assay, including gamma spectroscopy [22-24], neutron activation analysis (NAA) [24,25],

and inductively coupled plasma mass spectrometry (ICP-MS) [19-21,24,26]. Gamma spectroscopy and NAA are not ideally suited to rapid or accurate determinations. Gamma spectroscopy requires large quantities of material (frequently many kilograms) and prolonged counting times (often months) in many cases [20,24]. NAA doesn't require preliminary sample manipulation, but it is expensive and may create further complications by the formation of interfering radionuclides. ICP-MS is considered one of the most powerful analytical methods for trace and ultratrace analysis, offering subpicogram per milliliter detection limits for U and Th with minimal analysis time. However, matrix constituents are one of the main factors affecting detection limit. The high levels of matrix components can give rise to deposit on the sampler and skimmer cones of ICP-MS and reduce the response signal [19]. Thus, a dissolved sample may need to be diluted in order to lower its total dissolved solids content, which clearly degrades achievable detection limits. In practice, the most frequently used methods are separation of the analytes from the matrix through different methods, such as ion chromatography, coprecipitation, extraction and distillation [27-30]. However, due to the complexity of the process, many additional problems will arise, including increasing risk of contamination and extending the analysis time.

In the CUPID project, our laboratory is involved in the screening of Li_2MoO_4 crystal and raw material purity. For this purpose, an ICP-MS approach was selected. The detection ability, matrix influence and matrix separation method were investigated respectively. This was the first time that such a comprehensive assessment of ultratrace Th, U and K content in high-purity Li_2CO_3 had been made using ICP-MS. Meanwhile, to further confirm the reliability of the results, the results of NAA measurement were referenced.

Material and methods

Instrumentation and materials

An ICP-MS (Thermo Fisher X series) equipped with a cyclonic glass spray chamber and a pneumatic nebulizer was used in this work. Analytical balance (0.01 mg, METTLER TOLEDO AB265-S) was used to weigh samples. TEVA and UTEVA resin (100-150 μm , TRISKEM International) were used for extraction chromatography. 2 ml empty column tubes (Beijing UDLER Technologies) were used to fill resins. Polypropylene (PP) tubes (50 ml, Environmental Express) were used to dissolve sample. All dissolution, separation and dilution procedures were conducted in the class 100 fume hood and the 1000 clean room.

Chemicals and reagents

All acids used for the dissolution and separation procedures were of super analytical grade (HNO_3 , and H_2O_2 : TAMA Pure AA-10, Tama Chemical Inc; HCl : G6, Shanghai Aoban Technology). High-purity water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$) was obtained from a Milli-Q

Element water purification system (Millipore). The single element standard solutions (Th, U, K and Li) were purchased from SPEX CertiPrep.

Investigate of lithium matrix influence

High-concentration lithium standard solution (10000 $\mu\text{g g}^{-1}$) and Li_2CO_3 sample were diluted step by step to obtain the lithium matrix solution with different lithium contents (1 $\mu\text{g g}^{-1} \sim 8000 \mu\text{g g}^{-1}$). Th, U, and K standard solutions were added simultaneously. In the diluted solution, the final concentrations of Th, U, and K were approximately 1 ng g^{-1} . Through the recovery of Th, U and K, the influence of lithium and Li_2CO_3 matrix on Th, U and K was investigated.

Recovery correction method

About 1 g Li_2CO_3 sample was dissolved and diluted step by step, and the lithium concentration in the final sample ranges from 1 $\mu\text{g g}^{-1} \sim 8000 \mu\text{g g}^{-1}$. The specific concentration range can be determined based on the contents of Th, U and K in the actual samples. Each sample at every concentration level contained two aliquots. One serving as the sample solution, the other added with standard solutions of Th, U and K to evaluate the recovery.

The Th, U and K contents in the sample were calculated by the following formula.

$$\bar{x} = \frac{\sum_{i=1}^n c_i * f_i * r_i^{-1} * 100}{n} \quad (1)$$

Where \bar{x} (pg g^{-1}) was Th, U or K contents in the sample. C_i (pg g^{-1}) was the measured concentration of Th, U and K in a certain diluted Li_2CO_3 sample. f_i was dilution factor of a certain diluted Li_2CO_3 sample. r_i (%) was recovery of Th, U and K in a certain diluted Li_2CO_3 sample. n was the number of diluted Li_2CO_3 sample.

Separation and pre-concentration of TEVA-UTEVA combined resin

An approximate 2 g samples were mixed with 10 ml 8M HNO_3 in 50 ml PP tube. In order to prevent the violent reaction of the dissolution process, the samples were moistened with a small amount of water after weighing, and then dissolved by drip adding HNO_3 solution. After all the samples were dissolved, the solution came to the separation and pre-concentration process described mainly in Ref. [29].

TEVA and UTEVA resin was loaded into empty column tubes with a bed volume of 2mL and were prewashed with 5M HCl and 0.1M HCl, separately, then were

conditioned with 3M HNO₃. The sample solutions passed successively through TEVA and UTEVA. Th attached to the TEVA resins were eluted with 5 mL 5M HCl and U attached to the UTEVA resins were eluted with 5 mL 0.1M HCl. Mixed Th and U solutions added 0.5ml H₂O₂ and 0.5ml 3M HNO₃, then heated at 100°C for resin digestion and removing HCl. Then the solutions were weighted and used for Th and U measurement.

ICP-MS measurement

The measurement of Th and U were operated in standard mode. And the measurement of K was operated in standard mode and cool flame mode. Operating parameters are summarized in Table 1. No significant changes in day-to-day instrument performance were encountered during this work. Th, U and K were quantitatively measured by external standard method. Calibration solution concentrations of 0~10 ng g⁻¹ were used for Th, U and K matrix investigation and measurement of K in the actual sample. Calibration solution concentrations of 1~10 pg g⁻¹ were used for measurement of Th and U in the actual sample. The calibration solution and sample solution were measured in turn.

Table 1 ICP-MS operating conditions

Parameters	Standard mode	Standard mode	Cool flame mode
RF power	1300 W	1300 W	500W
Cool gas	14.0 L min ⁻¹	14.0 L min ⁻¹	14.0 L min ⁻¹
Auxiliary gas	0.91 L min ⁻¹	0.91 L min ⁻¹	0.90 L min ⁻¹
Nebulizer gas	0.85 L min ⁻¹	0.85 L min ⁻¹	0.90 L min ⁻¹
Sampling depth	130	130	380
Scanning mode	Peak jump	Peak jump	Peak jump
Sweeps per reading	160	350	350
Dwell time	10 ms	10 ms	10ms
Measured isotopes	²³² Th, ²³⁸ U	³⁹ K	³⁹ K

NAA measurement

For comparison, a Li₂CO₃ sample from the same production batch as those analyzed by ICP-MS was measured using NAA. A total of 4.98 g of Li₂CO₃ powder was placed in a clean polyethylene vial and irradiated with neutrons at the TRIGA Mark II research reactor in Pavia, Italy, for six consecutive hours. The irradiation was conducted alongside K, U, and Th standards for calibration purposes. After irradiation, the sample and standards were analyzed using gamma spectroscopy at the Radioactivity Laboratory of the Physics Department of University of Milano Bicocca, Italy, to detect the activated isotopes ⁴²K, ²³⁹Np, and ²³³Pa. These measurements were used to determine the concentrations of their respective precursors, ⁴¹K, ²³⁸U, and ²³²Th, in the powder. The concentration of ⁴⁰K was then determined from ⁴¹K by rescaling according to their respective isotopic abundances. A detailed discussion of the irradiation procedure and methods is beyond the scope of this paper. The

methodology employed in this measurement is thoroughly described in Ref. [31]. The results are reported in the next Section.

Results and discussion

Detection limit of ICP-MS

Since Li_2CO_3 was used as the raw material for the Li_2MoO_4 crystal, low contents of Th, U, and K were required. Therefore, the detection limits of the ICP - MS instrument itself needed to be evaluated first. In this work, 2%(V/V) HNO_3 was used as the evaluation solution, and the 3 times the standard deviation of the results of 10 parallel measurements was taken as the ICP-MS detection limit. The ICP-MS detection limit measurement results were shown in Table 2. The results showed that the ICP-MS detection limits of Th and U were 0.035 pg g^{-1} and 0.025 pg g^{-1} respectively. Therefore, this proved that the measurement of Th and U in ultrapure Li_2CO_3 by ICP-MS was feasible. In standard mode, the detection limit of K was 1.16 ng g^{-1} , while in cold flame mode, the detection limit of K was reduced by more than two orders of magnitude to 0.008 ng g^{-1} . When measuring K by ICP - MS, it was mainly interfered with by the plasma gas (Ar), namely the trailing of ^{40}Ar interferes with ^{39}K . In the cold flame mode, due to the low RF power, the ionization efficiency and background signal of Ar were reduced, while K was basically unaffected because of the low ionization energy, thus improving the detection ability. The results showed that compared with the standard mode, the cold flame mode was more suitable for the measurement of K in ultrapure Li_2CO_3 . The cold flame mode was adopted in subsequent work.

Table 2. Detection limit of the method and process blank.

Parameters	Th pg g^{-1}	U pg g^{-1}	K (Cool flame mode) ng g^{-1}	K (Standard mode) ng g^{-1}
<i>Detection limit</i>				
ICP-MS	0.035	0.025	0.008	1.16
Recovery correction method	5.54	3.94	7.53	/
TEVA-UTEVA method	0.178	0.155	/	/
<i>Process blank</i>				
TEVA-UTEVA method	0.365 ± 0.176	0.539 ± 0.168	/	/

Evaluation of lithium matrix influence

In the process of Li_2CO_3 sample dissolution, CO_2 escaped, and theoretically, the main matrix material of the solution was lithium ions. Therefore, the lithium matrix effect was first investigated using lithium single element standard solution. In addition, in order to further confirm the influence of Li_2CO_3 matrix, Li_2CO_3 samples were also

dissolved and diluted to be further investigated. Figure 1 showed that the influence of the matrix solution prepared with the Li_2CO_3 sample on Th, U and K was very close to the influence of the matrix solution prepared with the lithium standard solution, which demonstrated that the measurement of Th, U and K was mainly affected by the lithium matrix in Li_2CO_3 samples. With the increase of lithium concentration, the signals of Th, U and K were significantly suppressed. The suppression trends of Th and U were basically consistent with the increase in lithium concentration. However, there was a significant difference in the case of K. When the lithium concentration was less than $250 \mu\text{g g}^{-1}$, the recovery of Th and U was better than 70 %. Then the recovery rate declined rapidly. When the lithium concentration reached $8000 \mu\text{g g}^{-1}$, the recovery of Th and U decreased to 10 ~ 30%. The interference of the lithium matrix on the K signal was significantly greater than that on Th and U signals. When the lithium concentration was $250 \mu\text{g g}^{-1}$, the recovery of K had dropped to 10 ~ 20%. Moreover, within the lithium concentration range of 0 ~ $250 \mu\text{g g}^{-1}$, the results showed a continuous and significant decline in a large gradient. Since both Li and K were alkali metal elements with similar chemical properties and ionization energies, the lithium matrix caused such severe interference to K. In order to reduce the inhibition effect of lithium matrix, dilution was one option, but this method will greatly impair the detection ability of ICP-MS. Due to the significant differences in chemical properties between Li and Th/U, the separation of the lithium matrix was studied on measurement of Th and U in subsequent work. However, because Li and K had extremely similar chemical properties and K was highly prone to contamination, no further separation methods were employed in this work.

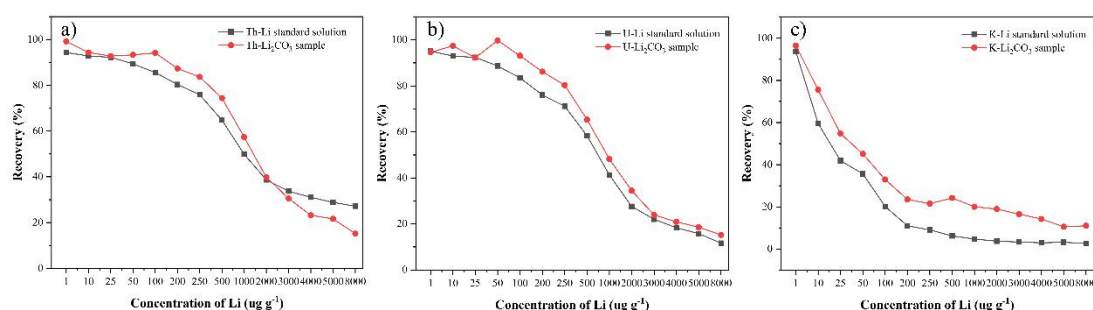


Figure.1 Relationship between Th, U and K recoveries and lithium matrix concentration. a) Th; b) U; c) K.

According to the detection limit of ICP-MS and recovery rate in different lithium matrices, the detection limit of recovery correction method can be evaluated by Eq.1. The specific results were also shown in Table 2, Th: 5.54 pg g^{-1} , U: 3.94 pg g^{-1} and K: 7.53 ng g^{-1} . The detection limit of this K is the lowest achievable in this work.

Influence of added concentrations of Th and U on recovery

In the recovery experiment, the amount of the standard solution added usually needs to be close to the content of the nuclide to be measured. However, due to the extremely low contents of Th and U in ultrapure Li_2CO_3 samples, the addition strictly

in accordance with the sample concentration will increase various uncertainties during the sample preparation and measurement processes. Therefore, the influence of added concentrations of Th and U on recovery were investigated.

Two different addition amounts of Th and U were evaluated. One addition amount was close to the content in the sample, about 5 pg g⁻¹. The other was much higher than the content in the sample, which was the routine detection content by ICP-MS, about 1 ng g⁻¹. For the addition amount of 5 pg g⁻¹, calibration curves of 0, 0.5, 1, 5, 10 pg g⁻¹ and 0, 0.5, 1, 2, 5, 10 ng g⁻¹ were used. For the addition amount of 1 ng g⁻¹, only the latter high concentration calibration curve was used. Figure 2 showed the obtained results of the recovery for two different addition amounts of Th and U. The obtained recovery rates were basically the same even when different calibration curves were used. This indicated that the recovery of Th and U were not affected by the added concentrations. This may be because within the range of 0~10 ng g⁻¹, the signal intensities of Th and U had very good linear relationships with the concentrations, as shown in Figure 3. Therefore, within this concentration range, the recovery was not affected by the concentration. This result indicated that in the recovery correction method, ng g⁻¹ level addition amounts of Th and U can be directly used to measure recovery (r_i). Therefore, there was no need to examine the actual concentration of Th and U in the ultrapure Li₂CO₃ sample, which greatly reduces the complexity and difficulty of the sample preparation and measurement processes.

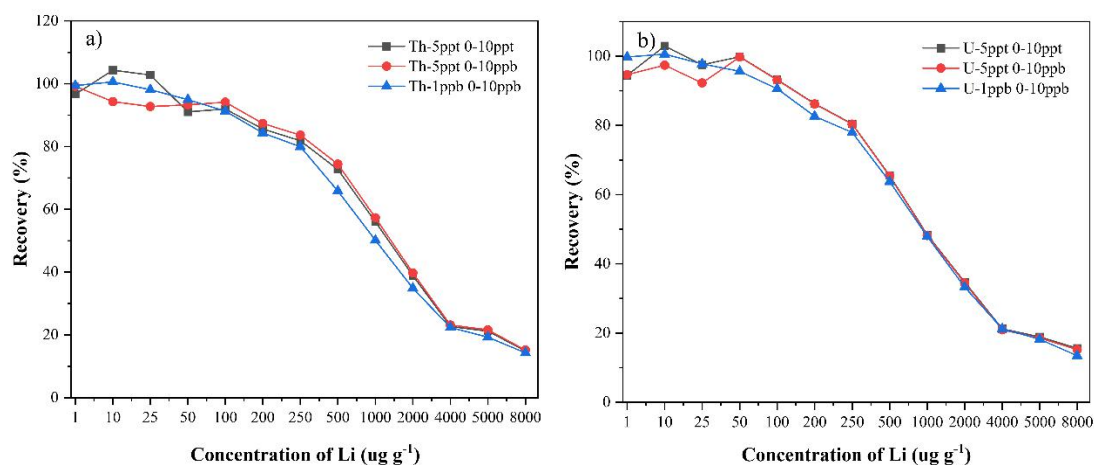


Figure 2 The recovery of two different addition amounts of Th and U. a) Th; b) U.

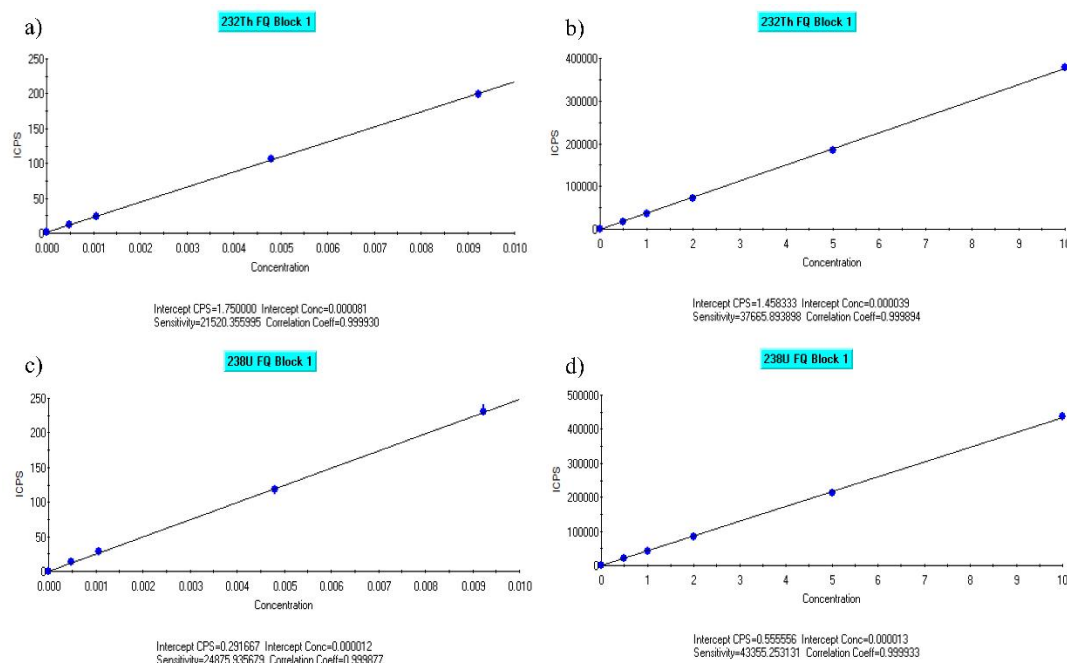


Figure 3 Two calibration curves with different concentration ranges. a) Th, 0~10 pg g^{-1} ; b) Th, 0~10 ng g^{-1} ; c) U, 0~10 pg g^{-1} ; d) U, 0~10 ng g^{-1} .

Evaluation of TEVA-UTEVA combined resin

UTEVA resin was widely used for the separation and pre-concentration of Th and U in samples and particularly suitable for U [19,20,32-35]. When UTEVA was used for Th, it was usually necessary to add oxalate reagents to eluate Th adsorbed by the resin [19,32]. This method increased the risk of Th and U contamination, and the literature showed that the recovery rate for Th was not good [19]. Yuan et al. [29] used both TEVA resin and UTEVA resin to separate Th and U in the copper samples and obtained a low detection limit. Considering that TEVA resin and UTEVA resin had good adsorption and elution characteristics for Th and U in the copper sample respectively, and only high purity acids (HNO_3 and HCl) are used in the process from sample loading to elution. So, this method was applied in this work.

Due to the complexity of the process of Th and U separation and pre-concentration method, process pollution and loss of Th and U were the key factors affecting the accuracy of the method. In this work, the process pollution was evaluated by process blank and detection limit of the method, and the process loss was evaluated by the recovery method due to the lack of suitable isotope tracers in our laboratory.

In the separation and pre-concentration process, the blanks, which included all reagents and were run in parallel with samples, were prepared simultaneously. By the blanks, the whole experimental background contamination from separation to measurement can be obtained. At the same time, the detection limit of the method can also be obtained based on the 3 times the standard deviation of the results of 10 parallel measurements of the blanks. The specific measurement results were also shown in Table 2. The results showed that after TEVA-UTEVA combined resin separation and pre-concentration process, the process blanks of Th and U were

significantly higher than the background of the instrument itself, and the detection limits were also significantly increased. The results indicated that contaminations of Th and U were introduced during the separation process, which maybe come from resin, containers and droppers. Throughout the experiment, all materials were disposable and without any treatment. Because process blank and the detection limit of separation method were still below the current requirement, the experimental background was not further reduced.

The blanks with Th and U standard solutions added were used to evaluate the separation and pre-concentration ability of TEVA-UTEVA combined resins. The specific results were shown in Figure 4. In the blank solution, the recovery of Th was between 100% ~102%, and the recovery of U was between 90% ~104%. The results showed that TEVA-UTEVA combined resins were good for the separation and pre-concentration of Th and U. In order to confirm the effect of lithium on TEVA-UTEVA combined resins, the recovery experiments of lithium standard solutions (10000 $\mu\text{g g}^{-1}$) with Th and U standard solutions added were carried out. The specific results were also shown in Figure 4. In lithium solution, the recovery results of Th and U were almost the same as that in blank solution, 95 ~99 % for Th and 96 ~102% for U, indicating that lithium had almost no effect on TEVA-UTEVA resins.

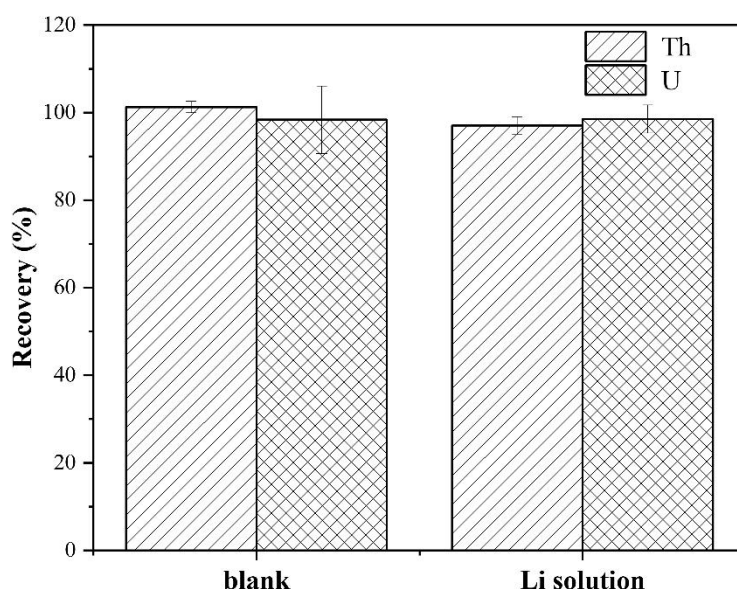


Figure 4. The recovery of Th and U obtained by adding standard solutions to the blank and Li matrix solution.

Analysis of Li_2CO_3 samples

One Li_2CO_3 sample, contents of Th and U were below the detection limit of ICP-MS when using a direct dilution (the content of lithium: $\sim 200 \mu\text{g g}^{-1}$) in preliminary measurement, was analyzed by recovery correction method and TEVA-UTEVA method respectively. In recovery correction method, the lithium concentration ranges from 500 ~ 8000 $\mu\text{g g}^{-1}$ for Th and U measurement and from 10 ~ 8000 $\mu\text{g g}^{-1}$ for K

measurement in the final solutions. The specific results were shown in Figure 5. The results indicated that, without recovery correction, the values of Th, U, and K in Li_2CO_3 decreased as the concentration of the lithium matrix increased. These results were consistent with those of the lithium matrix influence experiment. However, after being corrected with the recovery results, the values of Th, U and K in Li_2CO_3 fluctuated around the mean values at different concentrations of lithium matrix, which proved that the recovery correction could better offset the inhibition by lithium matrix.

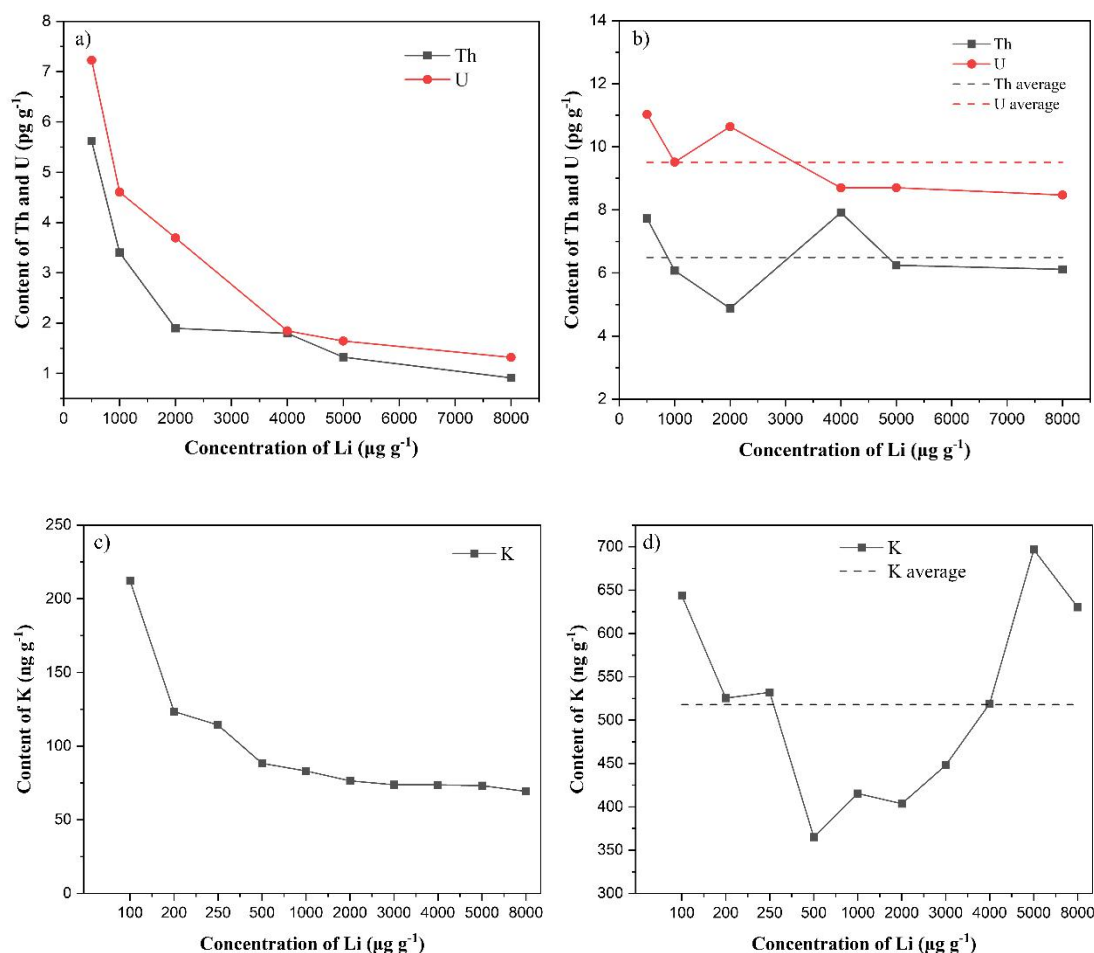


Figure 5 the results of Th, U and K in Li_2CO_3 sample by recovery correction method. a) Th and U contents without correction of recovery; b) Th and U contents after correction of recovery; c) K contents without correction of recovery; d) K contents after correction of recovery.

The analysis results of Th and U by different methods were summarized in Table 3. Although the NAA measurement could assess only upper limits, these are in good agreement with the results of ICP-MS analysis. In addition, the results of the two methods based on ICP-MS were basically consistent. The result of U was slightly higher by the recovery correction method. It may be due to the fact that after Li_2CO_3 was diluted, the concentration was close to the lower limit of the ICP-MS, resulting in a large measurement error.

Table 3. Analysis of Th and U in the Li₂CO₃ sample. (Results in pg g⁻¹, mean±SD)

sample	ICP-MS				NAA	
	Recovery correction method		TEVA-UTEVA method		Th	U
	Th	U	Th	U		
Li ₂ CO ₃	6.49±1.14	9.51±1.09	6.89±0.68	7.89±0.41	< 10	< 8

The analysis results of K were summarized in Table 4. The result of ⁴⁰K was obtained by NAA method, and the value of ^{nature}K was calculated according to the isotope abundance of ⁴⁰K (abundance of ⁴⁰K: 0.0120 %). The results showed that the measurement results of K by the NAA method were basically consistent with those by the ICP-MS method. The measurement results of the ICP - MS method had a relatively large standard deviation, which may be caused by various factors, including environmental pollution, recovery errors, argon interference, etc.

Table 4. Analysis of K in the Li₂CO₃ sample. (mean±SD)

sample	ICP-MS	NAA	
	K	⁴⁰ K	^{nature} K
	ng g ⁻¹	pg g ⁻¹	ng g ⁻¹
Li ₂ CO ₃	518±112	58.3±1.5	486±13

Conclusions

Two quantitative methods, recovery correction method and TEVA-UTEVA combined resin method, were developed and evaluated to determinate the content of U and Th at ppt levels in high-purity Li₂CO₃ samples by ICP-MS. Recovery correction method was a relatively simple and fast analytical process, but the detection limit was slightly higher, Th: 5.54 pg g⁻¹ and U: 3.94pg g⁻¹. It can be used to make an initial assessment of Th and U content in Li₂CO₃ samples. If the Th and U content cannot be detected by this method, TEVA-UTEVA combined resin method, although more complex, had a lower limit of detection, 0.178 pg g⁻¹ and U: 0.155pg g⁻¹, and could be used to further confirm. TEVA-UTEVA combined resin method was prone to affected by process contamination, and theoretically, if process contamination can be strictly controlled, the detection limit can be lower than the values obtained in this paper.

For the measurement of K by ICP - MS, compared with the standard mode, the cold flame mode with reduced RF power was significantly more suitable. In the cold flame mode, through the recovery correction method, the detection limit of K in Li₂CO₃

samples can be as low as 7.53 ng g^{-1} . Comparison with the results of the NAA method, using ICP - MS in cold flame mode with recovery correction was a relatively accurate and reliable method.

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